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(30)Priority

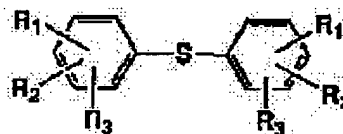
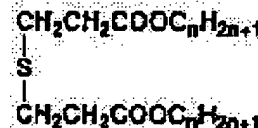
Priority number : 06 30724 Priority date : 01.03.1994 Priority country : JP

(54) ELECTROPHOTOGRAPHIC PHOTORECEPTOR

(57)Abstract:

PURPOSE: To stabilize characteristics over a long period of time by forming an electric charge transferring layer contg. a specified org. sulfur compd. as an antioxidant.

CONSTITUTION: A photosensitive layer formed on an electric conductive substrate is composed of an electric charge generating layer and an electric charge transferring layer contg. at least one kind of org. sulfur compd. represented by formula I or II as an antioxidant. In the formula I, (n) is a natural number of 3-25. In the formula II, each of R1 and R2 is H, halogen, alkoxy, etc., and R3 is hydroxy. The electric charge transferring layer preferably contains at least one kind of distyryl compd. and at least one kind of diamine compd. as electric charge transferring materials. It is preferable that the electric charge transferring layer further contains polycarbonate obtd. by copolymerizing bisphenol A with biphenyl as a binder.



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CLAIMS

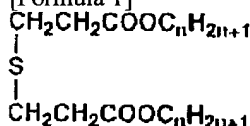
[Claim(s)]

[Claim 1] The photo conductor for electrophotography characterized by including as an antioxidant at least one sort of the organic-sulfur system compound in which the aforementioned charge transportation layer is shown by the following general formula (I) or the following general formula (II) by the sensitization layer formed on the conductive base consisting of a charge occurrence layer and a charge transportation layer at least.

[Claim 2] The photo conductor for electrophotography characterized by including at least one sort of the diamine compound shown by at least one sort and the following general formula (IV) of the ***** compound in which the aforementioned charge transportation layer is shown by the following general formula (III) in a photo conductor according to claim 1 as charge transportation matter.

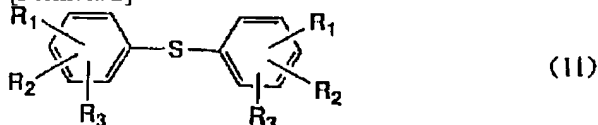
[Claim 3] The photo conductor for electrophotography characterized by including as a binder the bisphenol A-biphenyl copolymerization polycarbonate the aforementioned charge transportation layer is indicated to be with the following structure expression (V) in a photo conductor the claim 1 and given in two.

[Formula 1]



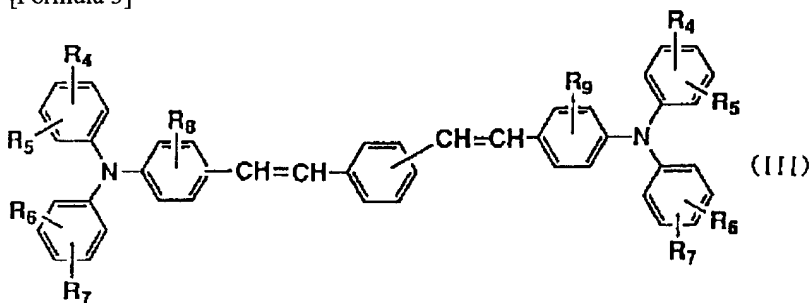
n in [formula expresses the natural number and the domain is 3 or 25.]

[Formula 2]



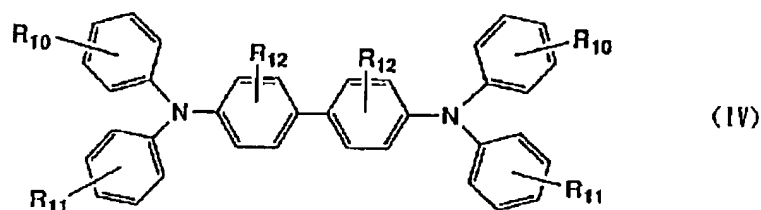
The inside R1 of [formula and R2 express a hydrogen atom, a halogen atom, an alkoxy group, the alkyl group that may be replaced, or an aryl group, and R3 expresses a hydroxyl.]

[Formula 3]



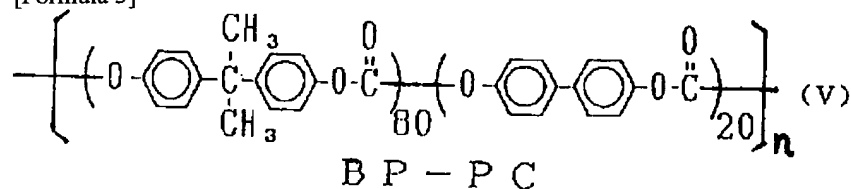
The inside R4 of [formula, R5, R6, and R7 express a hydrogen atom, a halogen atom, an alkoxy group, the alkyl group that may be replaced, or an aryl group, and R8 and R9 express a hydrogen atom, a halogen atom, an alkyl group, and an alkoxy group.]

[Formula 4]



The inside R10 and R11 of [formula expresses a hydrogen atom, a halogen atom, an alkoxy group, the alkyl group that may be replaced, or an aryl group, and R12 expresses a hydrogen atom, a halogen atom, an alkyl group, and an alkoxy group.]

[Formula 5]



The number in [formula and besides () expresses the proportion of the molecule of (), and n is an integer showing polymerization degree.]

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the antioxidant and charge transportation matter which are applied to the sensitization layer of the photo conductor for electrophotography, especially are used for a charge transportation layer, and a binder.

[0002]

[Description of the Prior Art] The photo conductor for electrophotography (a photo conductor is called below) takes the structure which carried out the laminating of the photo conductor layer which has a photoconduction function on a conductive base. The selectivity of a material is high, the organic photo conductor which contains an organic compound as a functional component which bears occurrence and transportation of a charge, and the laminating type organic photo conductor which comes to carry out the laminating of the stratum functionale, such as a charge occurrence layer and a charge transportation layer (electron hole transportation layer), especially are easy the functional design, its productivity by the coating method is high, and the application to the various printers including a copying machine is actively studied from an advantage, such as excelling in safety, in recent years. About the thing using the polycarbonate as an electron hole transportation layer binder, the photo conductor which was excellent in responsibility from the high hole mobility can be expected, using as the charge transportation matter (electron hole transportation matter) the ***** system compound which has especially the triphenylamine skeleton.

[0003] However, if this laminating type organic photo conductor is used on practical use conditions for a long time, problems, such as a fall of elevation and photographic sensitivity of a fall and rest potential of electrification potential, will occur. Some external factors can be mentioned as these causes. That is, it is the thing **ed by the ozone which occurs in electric discharge / electrification process, that outdoor daylight powerful at the time of a maintenance **s, etc. The influence which these external factors have on many above-mentioned properties leaves this photo conductor in the ozone ambient atmosphere, or can check it by the empirical method of irradiating the predetermined quantity of light.

[0004] The attempt of making a photo conductor contain the so-called additive known as an antioxidant or an ultraviolet ray absorbent that the above-mentioned problem should be solved is made variously. It is reported that the antioxidant which has the so-called phenol structure also in it is effective. For example, although there are JP,62-105151,A, JP,63-1836,A, etc., the present condition is that the technique in which all demand performances may still be satisfied is not established.

[0005]

[Problem(s) to be Solved by the Invention] Although an organic material has many advantages which are not in the charge of non-equipments as mentioned above, the present condition is that what fully satisfies all the properties simultaneously required of an organic photo conductor is not obtained, and when it is used especially on practical use conditions for a long time, the present condition is that problems, such as a fall of elevation and photographic sensitivity of a fall and rest potential of electrification potential, have occurred.

[0006] It is in this invention offering the photo conductor for electrophotography which realizes stabilization of the property over a long period of time by using the new organic material which is made in view of the aforementioned trouble and used for a sensitization layer until now as an antioxidant, the charge transportation matter, and a binder.

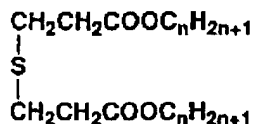
[0007]

[Means for Solving the Problem] According to this invention, the sensitization layer formed on the conductive base should consist of a charge occurrence layer and a charge transportation layer at least, and the above-mentioned purpose should contain as an antioxidant at least one sort of the organic-sulfur system compound in which the aforementioned charge transportation layer is shown by the following general formula (I) or the following general formula (II).

[0008] At least one sort of the diamine compound shown by at least one sort and the following general formula (IV) of the ***** compound in which the aforementioned charge transportation layer is shown by the following general formula (III) should be included as charge transportation matter. It is attained by including as a binder the bisphenol A-biphenyl copolymerization polycarbonate the aforementioned charge transportation layer is indicated to be with the following structure expression (V).

[0009]

[Formula 6]

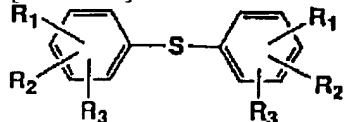


(I)

[0010] n in [formula expresses the natural number and the domain is 3 or 25.]

[0011]

[Formula 7]

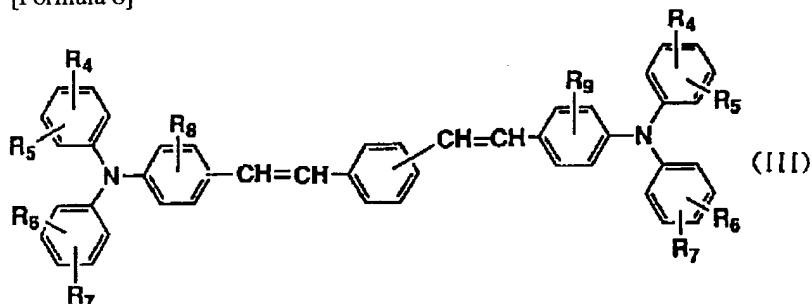


(II)

[0012] The inside R1 of [formula and R2 express a hydrogen atom, a halogen atom, an alkoxy group, the alkyl group that may be replaced, or an aryl group, and R3 expresses a hydroxyl.]

[0013]

[Formula 8]

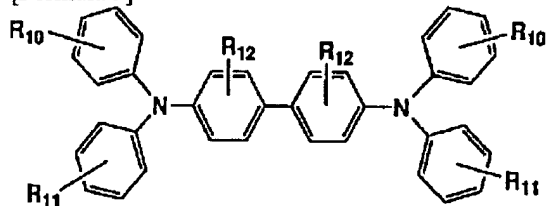


(III)

[0014] The inside R4 of [formula, R5, R6, and R7 express a hydrogen atom, a halogen atom, an alkoxy group, the alkyl group that may be replaced, or an aryl group, and R8 and R9 express a hydrogen atom, a halogen atom, an alkyl group, and an alkoxy group.]

[0015]

[Formula 9]

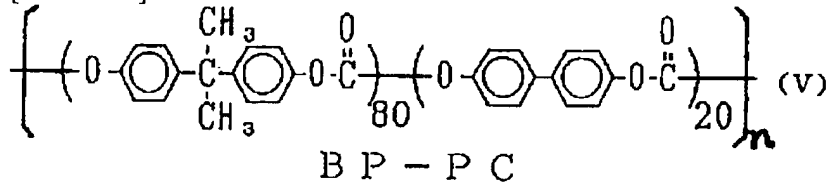


(IV)

[0016] The inside R10 and R11 of [formula expresses a hydrogen atom, a halogen atom, an alkoxy group, the alkyl group that may be replaced, or an aryl group, and R12 expresses a hydrogen atom, a halogen atom, an alkyl group, and an alkoxy group.]

[0017]

[Formula 10]



(V)

[0018] The number in [formula and besides () expresses the proportion of the molecule of (), and n is an integer showing polymerization degree.]

[0019]

[Function] In examining various organic materials zealously, in order that an artificer may attain the aforementioned purpose Although the technical elucidation is not yet enough made as a result of conducting much experiments about these compounds Even if it gave histories, such as neglect in the ozone ambient atmosphere, or strong light irradiation, to this photo conductor as an experiment fact, change was not looked at by a potential property or the photographic-sensitivity property, but even if it passed through the long-term use by actual electrophotography equipment, it was checked that there is no aging of a potential property or a photographic-sensitivity property. That is, it found out carrying out the work which prevents the thing to depend on the thing done for an oxidization degradation by the ozone which the organic material which forms this sensitization layer generates in an electrification process, or outdoor daylight powerful at the time of a maintenance **ing, and to do for a photodegradation.

[0020] Moreover, the technical knowledge which became clear for the first time by this invention is the fact that the organic-sulfur system (thioether system) antioxidant it is reported conventionally that the effect is is effective. Especially, as charge transportation matter, I understand that stabilization of the photo conductor property which stood high by adding this organic-sulfur system antioxidant is realized to what mixes and uses the ***** system compound and amine system compound which have the triphenylamine skeleton, and it is in it. When a bisphenol A-biphenyl copolymerization polycarbonate is furthermore used for a resin binder, it finds out that a stability improves by leaps and bounds.

[0021]

[Example] It explains, referring to a drawing about the example of this invention. Drawing 1 shows a negative electrification laminating type photo conductor, and consists of conductive base 1, charge occurrence layer 2, and a charge transportation layer 3. Drawing 2 shows a right electrification laminating type photo conductor, and consists of a conductive base 1, and charge transportation layer 3, charge occurrence layer 2 and a protection layer 4. Drawing 3 shows a right electrification monolayer type photo conductor, and consists of conductive base 1 and a sensitization layer 5.

[0022] The case where it applies to a negative electrification laminating type photo conductor below is explained. However, this example does not limit the generic claim of this invention. What gave surface modification by the thing to which the conductive base 1 carried out alumite processing of the front face of conductive base independence, such as a cylinder made from aluminum and a film made from a vacuum platings of aluminium, or this conductive base, or the resin coat is used. In this example, what washed and dried the cylinder base with the board thickness of 1mm made from aluminum, a length [of 310mm], and an outer diameter of 60mm as a conductive base 1 was used. The thing which made conductive polymers, such as insulating macromolecules, such as casein, polyvinyl alcohol, nylon, a polyamide, melanin, and a cellulose, or a poly-thiophene, polypyrrole, and a poly-aniline, or these macromolecules contain metallic-oxide powder and a low molecular weight compound as a material of the macromolecule variance coat used for surface modification is used.

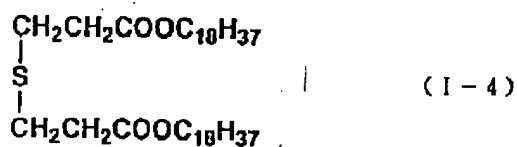
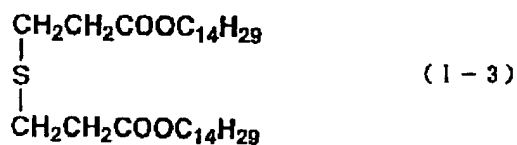
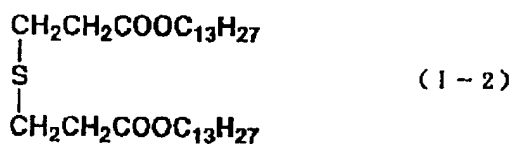
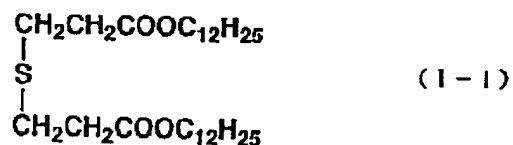
[0023] The charge occurrence layer 2 applies the material which distributed the grain of the charge occurrence matter in the resin binder, or is formed by technique, such as vacuum deposition, receives light, and generates a charge. Moreover, the injection nature to the charge transportation layer 3 of a charge which the charge occurrence luminous efficacy is high, and simultaneously generated is important, and it is desirable that the injection also by the low electric field has a good electric-field dependency few. As charge occurrence matter, colors, such as phthalocyanine compounds, such as a non-metal phthalocyanine and titanylphthalocyanine, various azo, a quinone, an indigo pigment or a cyanine, squarylium, *****, and a pyrylium compound, a selenium or a selenium compound, etc. is used, and the suitable matter can be chosen according to the light wave length field of the exposure light source used for image formation. As a subject, the charge transportation matter etc. is added to this and the charge occurrence layer 2 can also use the charge occurrence matter. As a resin binder, a polycarbonate, polyester, a polyamide, polyurethane, an epoxy polyvinyl butyral, a polyvinyl acetal, a phenoxy resin, silicone resin, acrylic resin, vinyl chloride resin, a vinylidene chloride resin, a vinyl acetate resin, a ***** resin, cellulosic resins or these copolymers and a halogenated compound, and cyanoethylation **** are used.

[0024] the charge transportation layer 3 -- the inside of a resin binder -- the organic charge transportation matter ***** -- the aforementioned general formula (III) the shown ***** system compound -- or -- (IV) the shown diamine system compound -- a simple substance -- or it combines and uses In a dark place, the charge of a photo conductor is held as an insulator layer, and the function to convey the charge poured in from a charge occurrence layer at the time of a photoreception is demonstrated. As a resin binder, a polycarbonate, polystyrene, polyphenylene-ether acrylic resin, etc. can be used.

[0025] Moreover, it is the aforementioned general formula as an antioxidant added in charge transportation matter application liquid. (I) Or the organic-sulfur system (thioether system) compound shown by (II) is used. The aforementioned general formula (I) It is as follows when the example of the compound shown is illustrated.

[0026]

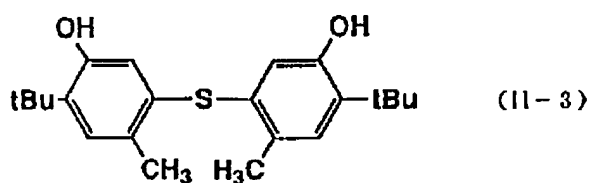
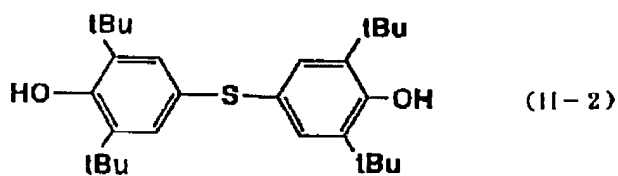
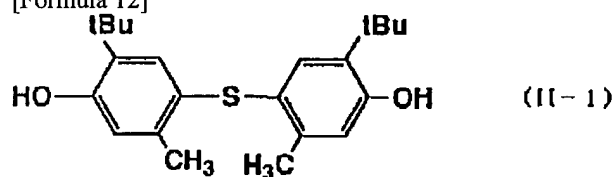
[Formula 11]



[0027] The aforementioned general formula (II) It is as follows when the example of the compound shown is illustrated.

[0028]

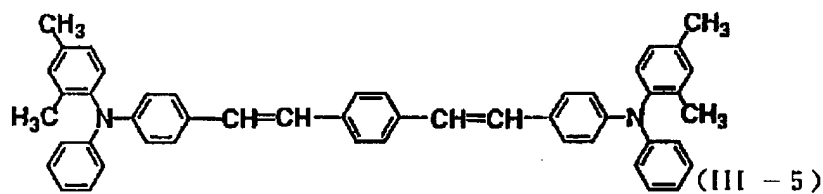
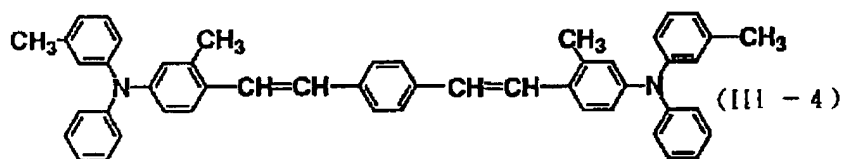
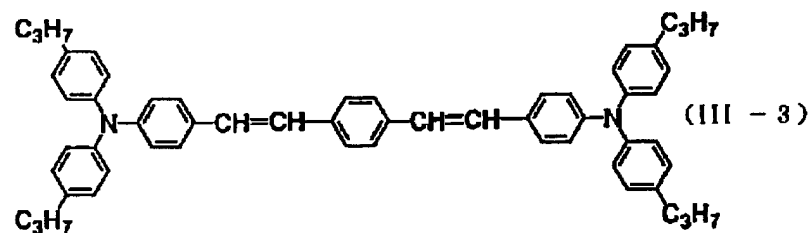
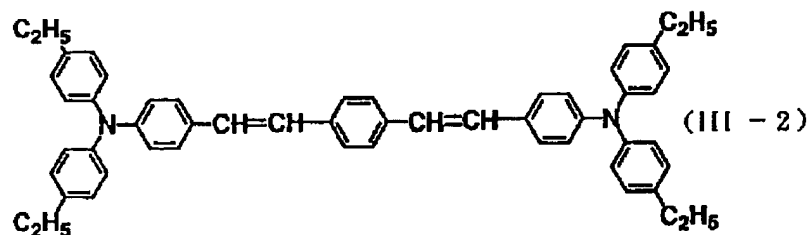
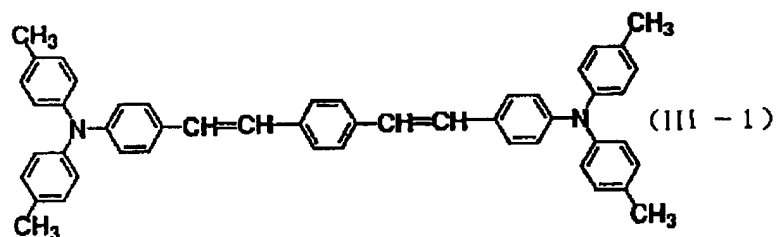
[Formula 12]



[0029] The aforementioned general formula (III) It is as follows when the example of the compound shown is illustrated.

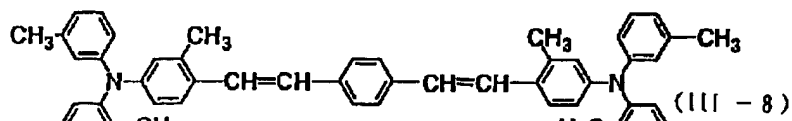
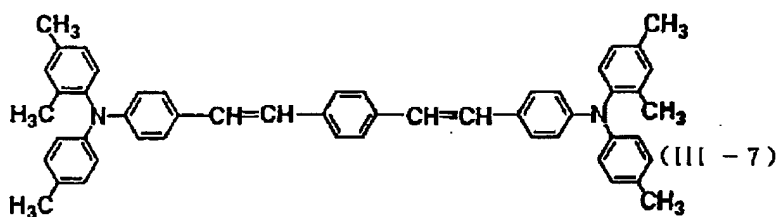
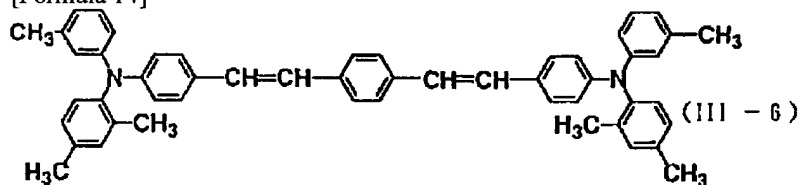
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[Formula 13]



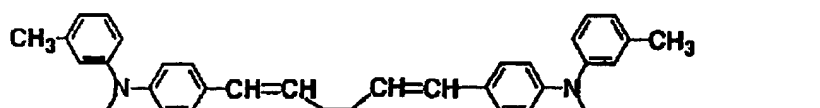
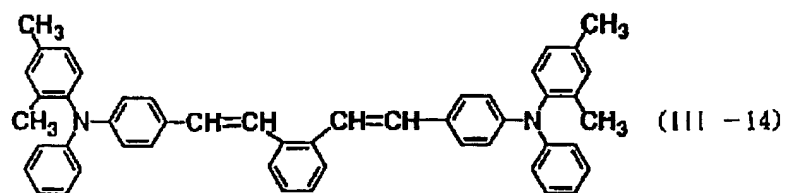
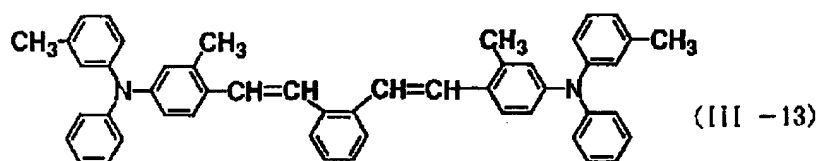
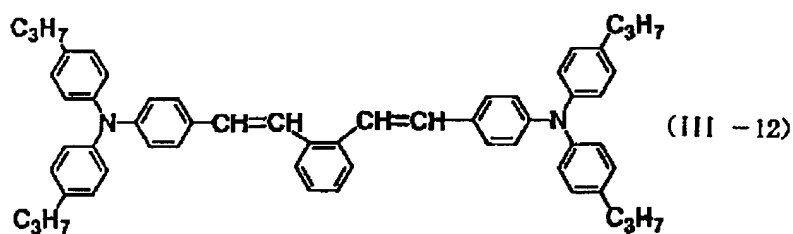
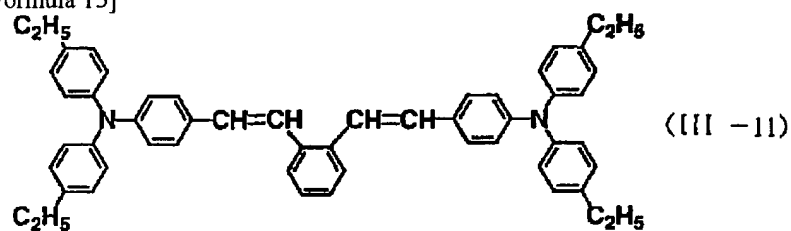
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[Formula 14]



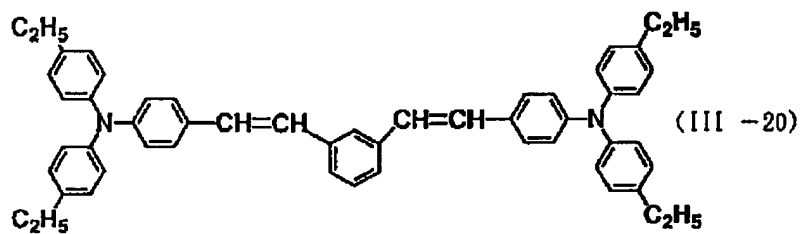
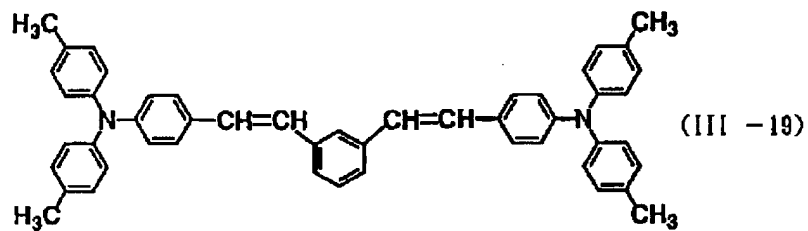
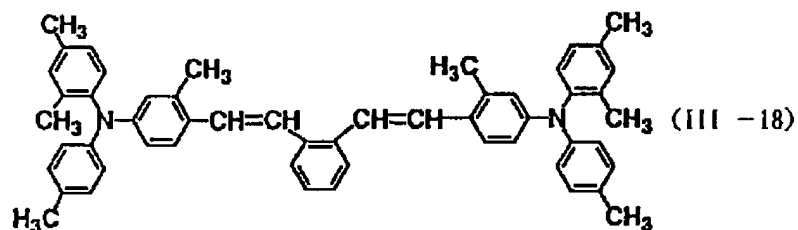
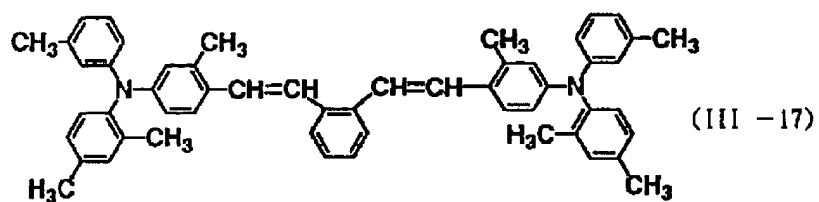
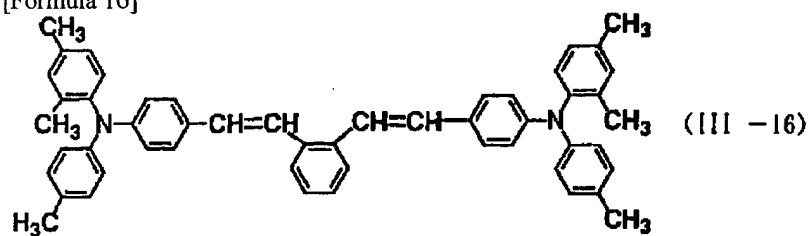
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[Formula 15]



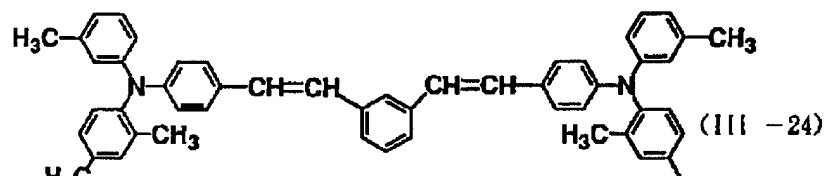
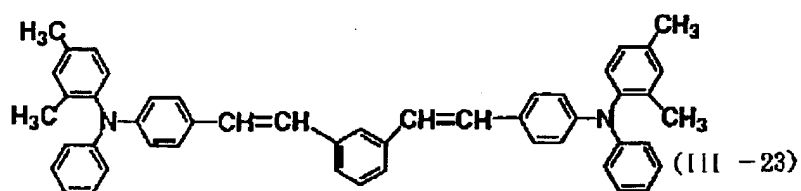
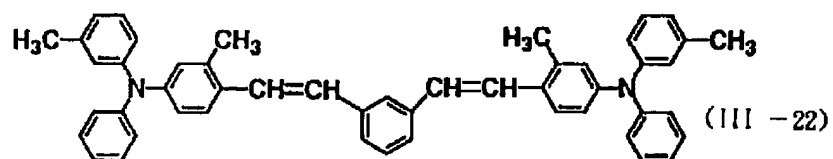
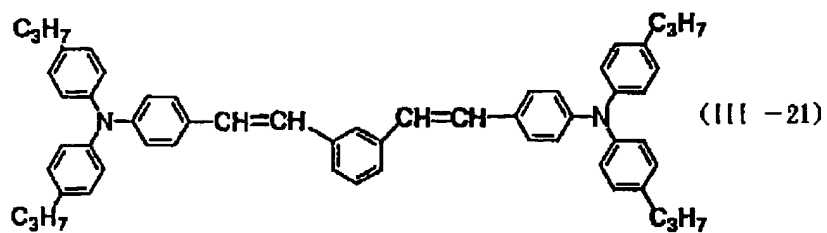
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[Formula 16]



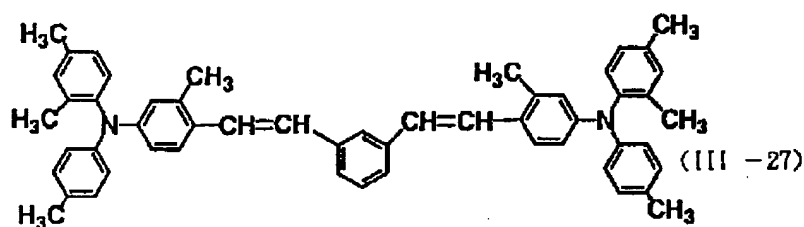
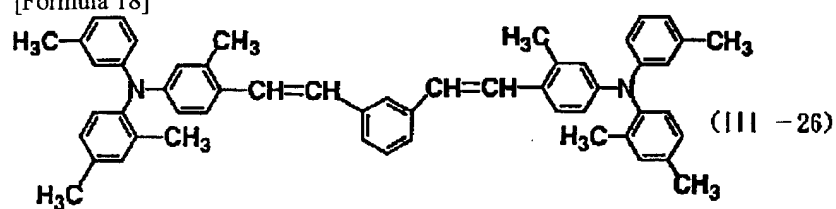
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[Formula 17]



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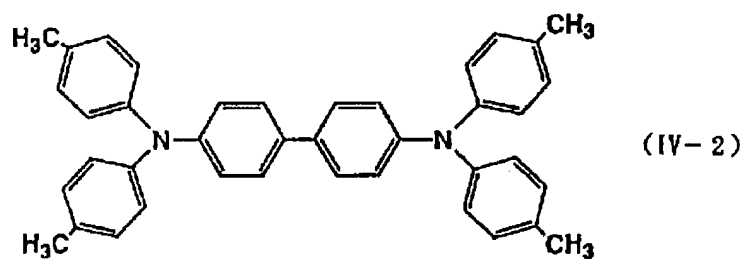
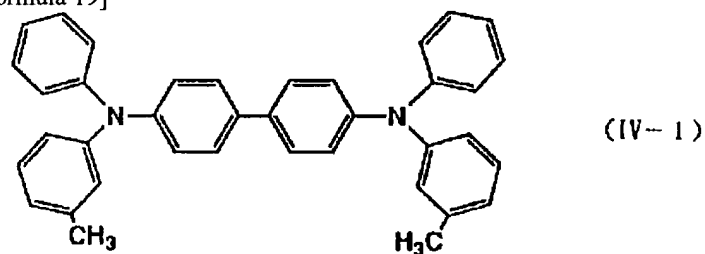
[Formula 18]



[0036] The aforementioned general formula (IV) It is as follows when the example of the compound shown is illustrated.

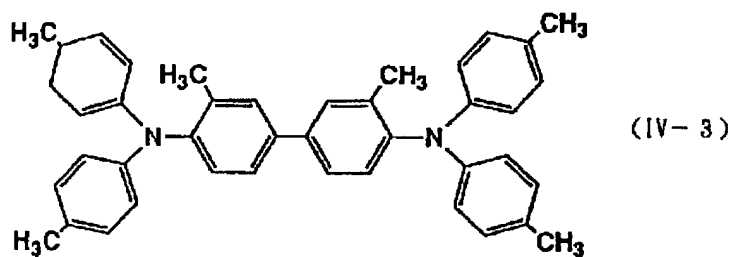
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[Formula 19]



[0038]

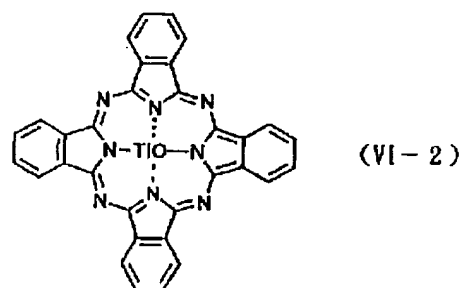
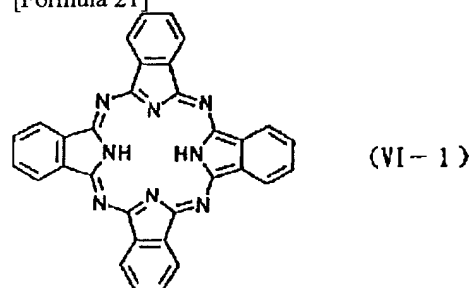
[Formula 20]



[0039] It is as follows when the example of the screw azo system compound used for the charge occurrence layer of this example is illustrated.

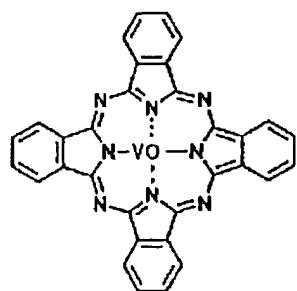
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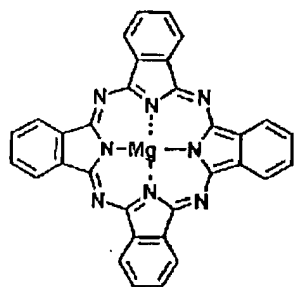


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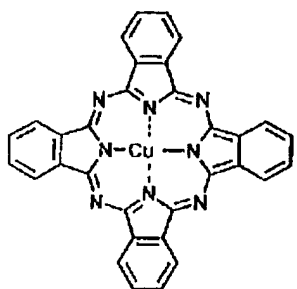
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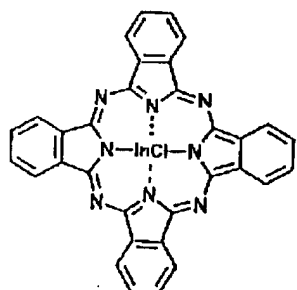
(VI-3)



(VI-4)

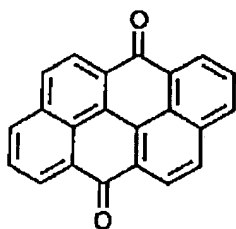


(VI-5)

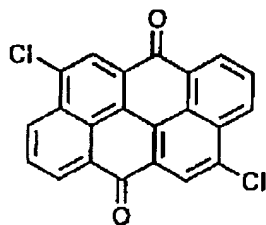


(VI-6)

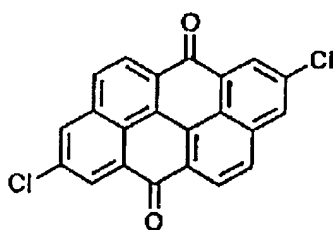
[0042]
[Formula 23]



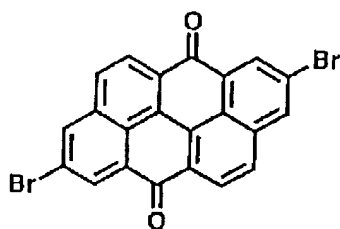
(VI-7)



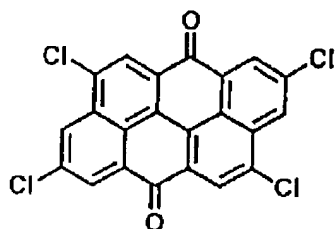
(VI-8)



(VI-9)

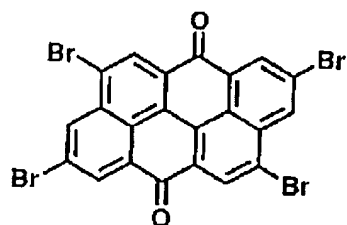


(VI-10)

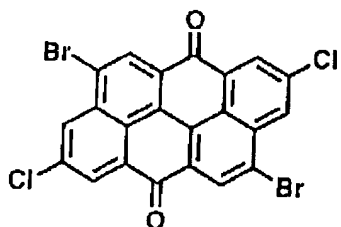


(VI-11)

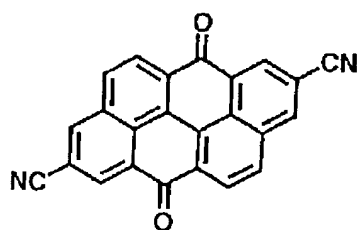
[0043]
[Formula 24]



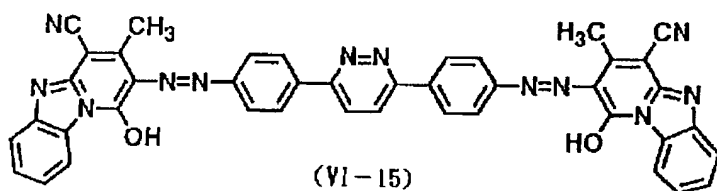
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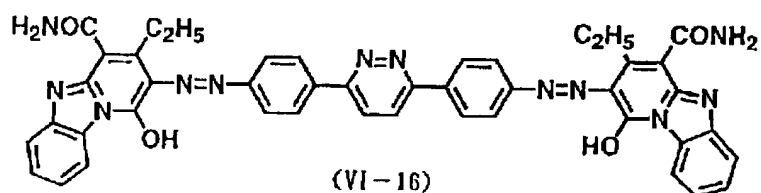
(VI-13)



(VI-14)



(VI-15)



(VI-16)

[0044]

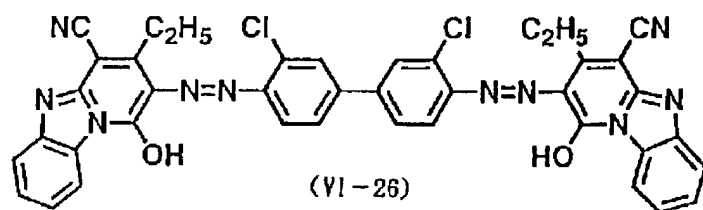
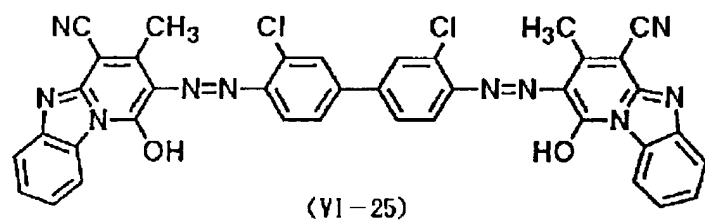
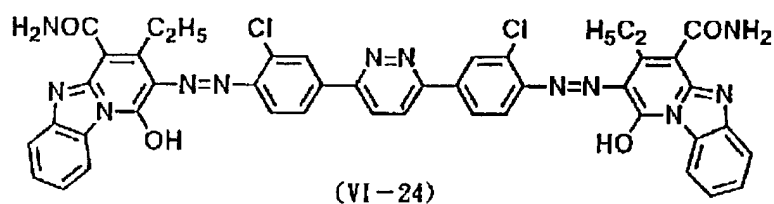
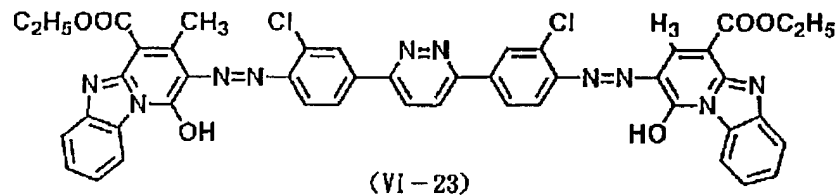
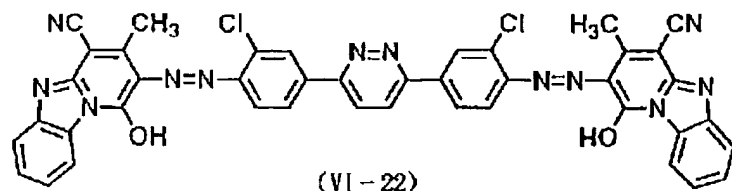
[Formula 25]

ID=000027

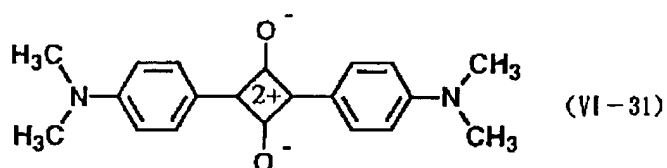
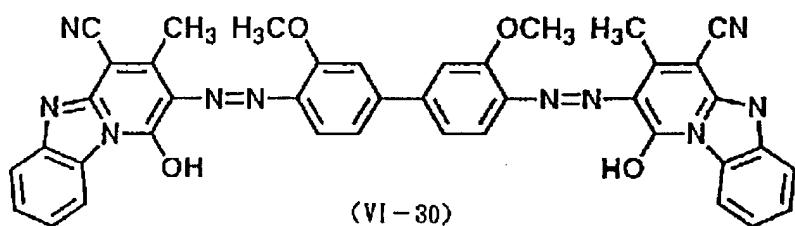
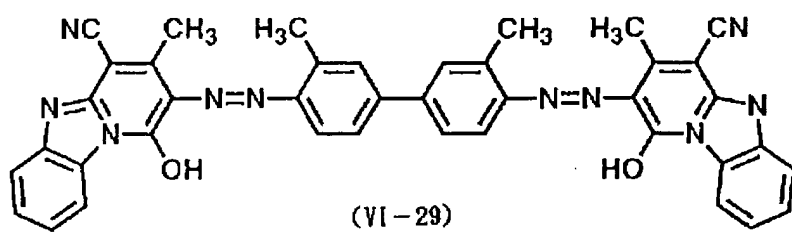
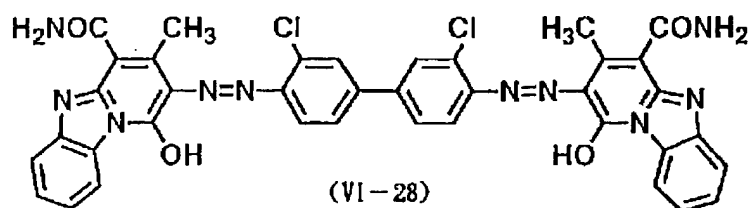
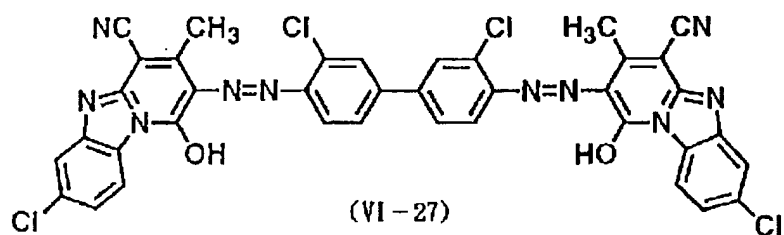


[0045]

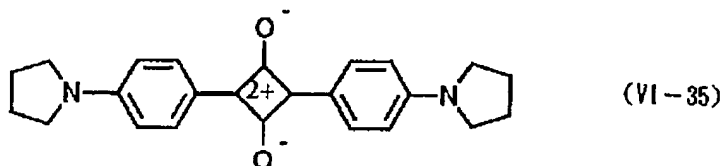
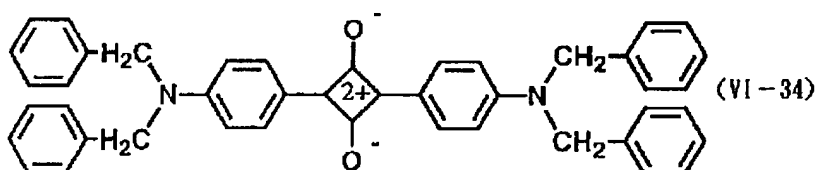
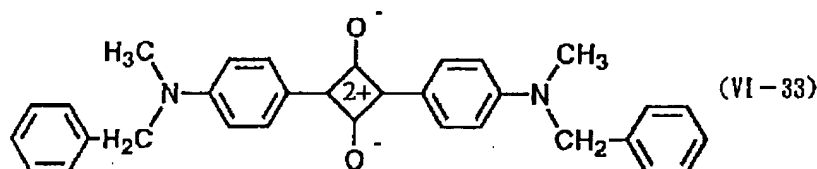
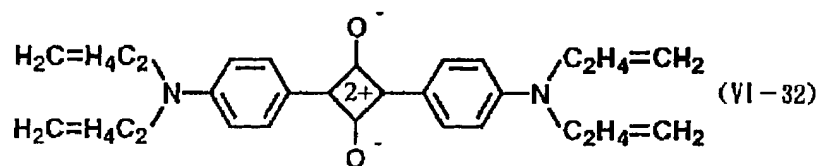
[Formula 26]



[0046]
[Formula 27]



[0047]
[Formula 28]



[0048] Using the resin coat application liquid which was melted in the mixed solvent of the methanol 200 weight section and the 1-butanol 100 weight section, and adjusted the polyamide (tradename:T171, product made from die cell-*****) 4 weight section of the [example 1] number average molecular weight 100,000, and the styrene-maleic resin (tradename:***** pearl AP, product made from BASFJapan Ltd.) 1 weight section, 0.1 micrometers of resin coats were formed by the dipping method on the conductive base 1, and the base material was

[0049] The diallyl-phthalate-resin (tradename:***** K, product made from Osaka soda) 1 weight section was mixed with the methyl-ethyl-ketone 150 weight section as the screw azo compound 1 weight section and the binder resin which are shown in aforementioned compound No. (VI-27) as charge occurrence matter, it kneaded with the mixed mixer for 3 hours, application liquid was adjusted, and it applied by the dipping method on the aforementioned base material, and the charge occurrence layer 2 was formed so that the thickness after xeransis might be set to 1 micrometer.

[0050] Thus, the compound 650 weight section shown as charge transportation matter on the obtained charge occurrence layer 2 at aforementioned compound No. (III-7), The compound 100 weight section shown in aforementioned compound No. (IV-1), the compound 250 weight section shown in aforementioned compound No. (IV-2), The bisphenol A-biphenyl copolymerization polycarbonate (tradename:BP-Pc, Idemitsu Kosan make) 1000 weight section shown in the aforementioned structure expression (V), As an antioxidant, the compound 15 weight section shown in aforementioned compound No. (I-4) was melted in the dichloromethane 700 weight section, charge transportation layer application liquid was adjusted and it applied by the dipping method, the charge transportation layer 3 was formed so that the thickness after xeransis might be set to 15 micrometers, and the photo conductor was produced.

The electrification transportation matter of the [example 2] example 1 was changed to compound No. (III-7), and the photo conductor was produced like the example 1 except considering as compound No. (III-13).

The electrification transportation matter of the [example 3] example 1 was changed to compound No. (III-7), and the photo conductor was produced like the example 1 except considering as compound No. (III-22).

The electrification transportation matter of the [example 4] example 1 was changed to compound No. (III-7), and the photo conductor was produced like the example 1 except considering as compound No. (III-26).

The antioxidant of the [example 5] example 1 was changed to compound No. (I-4), and the photo conductor was produced like the example 1 except considering as compound No. (II-1).

The antioxidant of the [example 6] example 2 was changed to compound No. (I-4), and the photo conductor was produced like the example 1 except considering as compound No. (II-1).

It changed to the bisphenol A-biphenyl copolymerization polycarbonate (tradename:BP-Pc, Idemitsu Kosan make) 1000 weight section as a binder in [example 7] charge transportation layer application liquid, and the photo conductor was produced like the

example 1 except blending the bisphenol Z polycarbonate (tradename-CZ300, Mitsubishi Gas Chemical make) 1000 weight section.

It changed to the bisphenol A-biphenyl copolymerization polycarbonate (tradename:BP-Pc, Idemitsu Kosan make) 1000 weight section as a binder in [example 8] charge transportation layer application liquid, and the photo conductor was produced like the example 1 except blending the bisphenol A polycarbonate (tradename : ***** light L-1225, Teijin formation make) 1000 weight section.

The photo conductor was produced like the example 1 except not blending the compound shown by compound No. (I-4) in [example 1 of comparison] charge transportation layer application liquid.

The photo conductor was produced like the example 2 except not blending the compound shown by compound No. (I-4) in [example 2 of comparison] charge transportation layer application liquid.

It changed to the compound shown by compound No. (I-4) in [example 3 of comparison] charge transportation layer application liquid, and the photo conductor was produced like the example 1 except carrying out 40 weight section combination of the ***** phenolic compound shown in the following structure expression (VII).

It changed to the compound shown by compound No. (I-4) in [example 4 of comparison] charge transportation layer application liquid, and the photo conductor was produced like the example 2 except carrying out 40 weight section combination of the ***** phenolic compound shown in the following structure expression (VII).

The photo conductor was produced like the example 7 except not blending the compound shown by compound No. (I-4) in [example 5 of comparison] charge transportation layer application liquid.

The photo conductor was produced like the example 8 except not blending the compound shown by compound No. (I-4) in [example 6 of comparison] charge transportation layer application liquid.

[0051]

[Formula 29]

Fig-000031



[0052] Thus, the electrophotography property of the obtained photo conductor was evaluated. Various kinds of photo conductors are carried in the copying machine or LASER beam printer which fixed the output of an electrification device, an exposure device, and an electric discharge device in order to evaluate the potential change at the time of continuous duty. The running examination of 50,000 sheets of A3 forms was performed in the ambient atmosphere of ordinary temperature normal relative humidity (20 degree C and 60RH), and each potential variation at the time of a running end (delta Vw, delta Vb) was measured for the blank paper potential (Vw) and black paper potential (Vb) at the time of running start after measurement.

[0053] Moreover, each photo conductor was exposed to the bottom of the environment of 100 ppm of ozone levels for 4 hours in order to evaluate ozone-proof nature, and the reduction-by-half light exposure before and behind exposure was measured and measured. The light of 1000 (lx) was irradiated for 1 hour at each photo conductor in order to carry out ****-proof fatigability evaluation furthermore, and the electrification potential variation after measurement and an irradiation end (delta Vs) was measured for the initial electrification potential before the irradiation under a fixed electrification condition (Vs). These results are shown in Table 1.

[0054]

[Table 1]

	ランニング試験結果				オゾン試験結果		強光照射試験結果	
	初期電位		変化量		半減露光量 ($1 \times s$)		初期電位	変化量
	V _w (V)	V _b (V)	ΔV_w (V)	ΔV_b (V)	暴露前	暴露後	V _s (V)	ΔV_s (V)
実施例 1	-47	-605	5	5	0.65	0.66	-627	1
実施例 2	-45	-603	4	5	0.63	0.64	-624	-1
実施例 3	-45	-605	3	3	0.64	0.64	-624	-2
実施例 4	-44	-603	5	-1	0.62	0.63	-623	2
実施例 5	-48	-604	7	2	0.63	0.65	-626	-1
実施例 6	-47	-605	8	3	0.62	0.64	-625	4
実施例 7	-45	-607	11	-9	0.63	0.67	-626	15
実施例 8	-45	-605	15	-11	0.64	0.69	-626	21
比較例 1	-45	-610	45	-165	0.83	0.88	-645	-154
比較例 2	-46	-608	12	-120	0.70	0.79	-623	-150
比較例 3	-45	-605	2	-35	0.65	0.71	-626	-120
比較例 4	-44	-609	7	-64	0.66	0.73	-624	-130
比較例 5	-45	-608	50	-145	0.82	0.86	-628	-158
比較例 6	-44	-607	42	-170	0.79	0.87	-630	-181

As for the photo conductor which does not contain aforementioned compound No. (I-4) or (II-1) the shown organic-sulfur system (thioether system) compound at all, a photo conductor property falls remarkably by ozone exposure or strong light irradiation, and the potential change by running examination with the system has deviated from the practical use domain so that clearly from the above result. Moreover, as a result of comparing with a ***** phenolic compound, the organic-sulfur system compound showed the predominance which stood high about the stability of photographic sensitivity and electrification ability, so that clearly from the result of an example 1 and the examples 3-4 of a comparison. Moreover, it is checked that the organic-sulfur system compound concerning this invention can demonstrate the result in extensive structure and the organic photo conductor of material composition from the result of examples 1-8. Moreover, the stability which stood high when a bisphenol A-biphenyl copolymerization polycarbonate was used for a resin binder so that the result of an example 1 and the examples 7-8 may show was shown.

[0055]

[Effect of the Invention] According to this invention, at least one sort of the organic-sulfur system compound shown by the aforementioned general formula (I) or (II) as a charge transportation layer formed on a conductive base is included as an antioxidant. At least one sort of the ***** compound shown by the aforementioned general formula (III), Suppose that at least one sort of the diamine compound shown by the following general formula (IV) is included as charge transportation matter. By including as a binder the bisphenol A-biphenyl copolymerization polycarbonate furthermore shown with the aforementioned structure expression (V) An effect which was stated to the example is acquired, there is no property change under the ozone ambient atmosphere or strong light irradiation, and it is enabled to produce the photo conductor for electrophotography which is excellent in the property stability in the continuous duty over a long period of time.

[Translation done.]